



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<b>(51) International Patent Classification <sup>6</sup> :</b> <b>B41M 5/00</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 97/01448</b> <b>(43) International Publication Date:</b> 16 January 1997 (16.01.97)
<b>(21) International Application Number:</b> PCT/US96/10939 <b>(22) International Filing Date:</b> 26 June 1996 (26.06.96)  <b>(30) Priority Data:</b> 08/495,384      28 June 1995 (28.06.95)      US  <b>(71) Applicant:</b> KIMBERLY-CLARK CORPORATION [US/US]; 401 North Lake Street, Neenah, WI 54956 (US).  <b>(72) Inventors:</b> STOKES, Bruce, George; 86 Farmington Drive, Woodstock, GA 30188 (US). HARRIS, Linda, Garner; 1917 DeWinton Place, Lawrenceville, GA 30243 (US). KRONZER, Francis, Joseph; 4217 North Mountain Road, Marietta, GA 30066 (US).  <b>(74) Agents:</b> MAYCOCK, William, E. et al.; Kimberly-Clark Corporation, 401 North Lake Street, Neenah, WI 54956 (US).		<b>(81) Designated States:</b> AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).  <b>Published</b> <i>With international search report.</i> <i>Before the expiration of the time limit for amending the</i> <i>claims and to be republished in the event of the receipt of</i> <i>amendments.</i>
<b>(54) Title:</b> SUBSTRATE FOR INK JET PRINTING HAVING A MONOLAYER INK-RECEPTIVE COATING  <b>(57) Abstract</b>  A coated substrate which includes a first and second layer. The first layer has first and second surfaces. For example, the first layer may be a film or a nonwoven web. Desirably, the first layer will be a cellulosic nonwoven web. The second layer overlays the first surface of the first layer. The second layer may be composed of from about 20 to about 60 percent by weight of a latex binder, from about 20 to about 80 percent by weight of a hydrophilic silica, from about 1 to about 12 of a cationic polymer, and from about 0.5 to about 5 percent by weight of a surfactant, in which all percents by weight are based on the total dry weight of the second layer. The second layer also has a pH of from about 2 to about 6.		

**FOR THE PURPOSES OF INFORMATION ONLY**

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

**SUBSTRATE FOR INK JET PRINTING HAVING  
A MONOLAYER INK-RECEPTIVE COATING**

**Background of the Invention**

5

The present invention relates to a coated substrate.

10 Ink jet printing is an important printing technology capable of producing full-color, high quality images at high speed and low cost. For example, ink jet printing is capable of producing a full-color hard copy of computer-generated drawings or graphics. Consequently, ink jet printing is a rapidly growing technology which is gaining acceptance in general use. Ink jet printing also is expanding into wide format printing to produce large prints and banners.

15 Current ink jet printing technology involves forcing ink drops through small nozzles by piezoelectric pressure or by oscillation onto the surface of a substrate. An aqueous ink of low viscosity consisting of direct dyes or acid dyes is commonly used in ink jet printing. Once applied to a substrate, the ink droplet ideally will dry in the shape of a perfect circle, forming a single dot. The ink droplet needs to dry quickly without migrating into the surrounding area which would result in blurred or fuzzy printing. This migration of an ink droplet is called "feathering" or  
20 "bleeding". Therefore, the surface of the substrate should be very absorbent to facilitate rapid drying of the ink.

There are a large number of references which relate to ink jet printable substrates. The typical substrate is a paper or other material having an ink-receptive coating. The coating typically includes one or more pigments and a binder. Pigments which have been used, alone or in combination, include, by way of illustration only, silica; clay; calcium carbonate; talc; barium sulfate; diatomaceous earth; titanium dioxide; cation-modified non-spherical colloidal silica, in  
30 which the modifying agent is aluminum oxide, hydrous zirconium oxide, or hydrous tin oxide; calcium carbonate-compounded silica; prismatic orthorhombic aragonite calcium carbonate;

alumina; aluminum silicate; calcium silicate; kaolin; magnesium silicate; magnesium oxalate; magnesium-calcium carbonate; magnesium oxide; magnesium hydroxide; high-swelling montmorillonite clay; amorphous silica particles  
5 having a coating of a Group II metal; synthetic silica; and micro-powder silica. In some instances, the pigment may have certain defined requirements, such as particle diameter, oil absorption, surface area, water absorption, refractive index, and solubility in water.

10 Various binders have been employed to form the ink-receptive coating. Examples of such binders include, again by way of illustration only, a mixture of esterified starch and a water-insoluble cationic polymer; an epoxy resin and a thermoplastic resin; acrylic resins and other water-soluble  
15 polymers; a mixture of an alkylquaternaryammonium (meth)acrylate polymer and an alkylquaternaryammonium (meth)acrylamide polymer; poly(vinyl alcohol); a mixture of an acrylic resin and poly(vinyl alcohol); polyvinylpyrrolidone or vinylpyrrolidone-vinyl acetate copolymer or mixture thereof; an amine  
20 salt of a carboxylated acrylic resin; oxidized or esterified starch; derivatized cellulose; casein; gelatin; soybean protein; styrene-maleic anhydride resin or derivative thereof; styrene-butadiene latex; and poly(vinyl acetate).

Additional materials have been included in the ink-receptive layer, such as a cationic polymer. Moreover, two  
25 or more layers have been employed to form the ink-receptive coating.

Notwithstanding the improvements which have been made in substrates for ink jet printing, there is an opportunity for  
30 providing a high quality printed image on a substrate that is water resistant.

#### Summary of the Invention

35 The present invention addresses some of the difficulties and problems discussed above by providing an ink jet printable coated substrate which is particularly useful with colored

water-based ink jet inks. The coated substrate of the present invention gives sharp prints of brilliant color without feathering. In addition, the printed images will not bleed when exposed to moisture or water.

5       The coated substrate of the present invention includes a first and second layer. The first layer has first and second surfaces. For example, the first layer may be a film or a nonwoven web. Desirably, the first layer will be a cellulosic nonwoven web. The second layer overlays the first  
10       surface of the first layer. The second layer is composed of from about 20 to about 60 percent by weight of a latex binder, from about 20 to about 80 percent by weight of a hydrophilic silica, from about 1 to about 12 percent by weight of a cationic polymer, and from about 0.5 to about 5 percent by  
15       weight of a surfactant, in which all percents by weight are based on the total dry weight of the second layer.

      The second layer will have a pH of from about 2 to about 6. In addition, the hydrophilic silica generally will have an average particle size no greater than about 20 micrometers.  
20       For example, the average particle size of the hydrophilic silica typically will be from about 1 to about 20 micrometers. In addition, the hydrophilic silica generally will have a pore volume greater than 0.4 cubic centimeters per gram (cc/g). As an example, the pore volume of the hydrophilic silica may  
25       be from about 1 to about 2 cc/g.

      If desired, a third layer may overlay the second surface of the first layer. For example, such a layer may be what often is referred to in the papermaking art as a backsize layer. As another example, the third layer may be a tie coat,  
30       i.e., a coating designed to bind a pressure-sensitive adhesive to the second surface of the second layer. Alternatively, the third layer itself may be a pressure-sensitive adhesive. When the third layer is a tie coat, a fifth layer consisting of a pressure-sensitive adhesive and overlaying the third layer  
35       also may be present.

      Moreover, a fourth layer may be present between the first surface of the first layer and the second layer. An example

of such a layer is what is known in the papermaking art as a barrier layer.

### Detailed Description of the Invention

5

As used herein, the term "nonwoven web" is meant to include any nonwoven web, including those prepared by such melt-extrusion processes as meltblowing, coforming, and spunbonding. The term also includes nonwoven webs prepared by air laying or wet laying relatively short fibers to form a web or sheet. Thus, the term includes nonwoven webs prepared from a papermaking furnish. Such furnish may include only cellulose fibers, a mixture of cellulose fibers and synthetic fibers, or only synthetic fibers. When the furnish contains only cellulose fibers or a mixture of cellulose fibers and synthetic fibers, the resulting web is referred to herein as a "cellulosic nonwoven web." Of course, the paper also may contain additives and other materials, such as fillers, e.g., clay and titanium dioxide, as is well known in the papermaking art.

The term "latex binder" is used herein to mean a dispersion of water-insoluble polymer particles in water. The term "polymer" is intended to encompass both homopolymers and copolymers. Copolymers may be random, block, graft, or alternating polymers of two or more monomers. The polymer typically is a film-forming polymer, such as, by way of illustration only, polyacrylates, styrene-butadiene copolymers, ethylene-vinyl acetate copolymers, nitrile rubbers, poly(vinyl chloride), poly(vinyl acetate), ethylene-acrylate copolymers, and vinyl acetate-acrylate copolymers. Latex binders are well known to those having ordinary skill in the art.

As used herein, the term "cationic polymer" is meant to include any water-soluble polymer containing cationic functional groups. For example, the cationic polymer may be an amide-epichlorohydrin polymer, a polyacrylamide with cationic functional groups, polyethyleneimine, polydiallyl-

amine, a quaternary polycationic synthetic organic polymer, or the like.

The term "hydrophilic silica" is used herein to mean any amorphous hygroscopic silica having a hydrophilic surface. 5 The hydrophilic surface may be the natural hydrophilic surface characteristic of silica. For example, the silica may be a fumed silica or a precipitated silica. The silica surface may be modified, if desired, provided the modifying agent is hydrophilic. As another example, the silica may be a 10 naturally occurring silica, such as a diatomaceous earth. An example of a diatomaceous earth silica is Celite® 321 (Manville Products Corporation, Denver, Colorado). In general, the average particle size of the silica will be no greater than about 20 micrometers. As practical matter, the 15 average particle size of the silica typically will be in a range of from about 1 to about 20 micrometers. For example, the average particle size may be from about 2 to about 13 micrometers. As another example, the average particle size may be from about 3 to about 9 micrometers.

20 As used herein, the term "surfactant" has its usual meaning. In general, the surfactant may be a nonionic or a cationic surfactant. Desirably, the surfactant will be a nonionic surfactant, such as an alkylaryl polyether. For example, the surfactant may be a polyethoxylated alkylphenol.

25 The coated substrate of the present invention includes a first layer and second layer. The first layer has first and second surfaces. For example, the first layer may be a film or a nonwoven web. Desirably, the first layer will be a cellulosic nonwoven web. For example, the first layer may 30 be a polymer-reinforced paper, sometimes referred to as a latex-impregnated paper. As another example, the first layer may be a bond paper, i.e., a paper composed of wood pulp fibers and cotton fibers. The basis weight of the first layer typically will vary from about 40 to about 300 grams per 35 square meter (gsm). For example, the basis weight of the first layer may be from about 50 to about 250 gsm. As a

further example, the basis weight of the first layer may be from about 50 to about 200 gsm.

The second layer overlays the first surface of the first layer. As stated earlier, the second layer is composed of a latex binder, a hydrophilic silica, a cationic polymer, and a surfactant.

In general, the amount of latex binder may be from about 20 to about 60 percent by weight. For example, the amount of latex binder may be from about 25 to about 40 percent by weight. As another example, the amount of latex binder may be from about 25 to about 35 percent by weight. As already noted, the latex binder may be, by way of illustration only, a polyacrylate, styrene-butadiene copolymer, ethylene-vinyl acetate copolymer, nitrile rubber, poly(vinyl chloride), poly(vinyl acetate), ethylene-acrylate copolymer, or vinyl acetate-acrylate copolymer. Ethylene-vinyl acetate copolymers have been found to be particularly useful as binders.

The amount of hydrophilic silica present in the second layer typically will be from about 20 to about 80 percent by weight. By way of example, the amount of hydrophilic silica may be from about 30 to about 70 percent by weight. As another example, the amount of hydrophilic silica may be from about 50 to about 70 percent by weight.

The hydrophilic silica generally will have an average particle size no greater than about 20 micrometers and a pore volume greater than 0.4 cc/g. As an example, the average particle size may be from about 1 to about 20 micrometers. As another example, the average particle size may be from about 2 to about 13 micrometers. As an additional example, the average particle size of the hydrophilic silica may be from about 3 to about 9 micrometers. Also by way of example, the pore volume may be from about 1.2 to about 1.9 cc/g. As a further example, the pore volume may be from about 1.2 to about 1.7 cc/g.

The second layer also will contain from about 1 to about 12 percent by weight of a cationic polymer. For example, the amount of cationic polymer may be from about 2 to about 8



percent by weight. As another example, the amount of cationic polymer may be from about 3 to about 6 percent by weight. Cationic amine-epichlorohydrin copolymers and quaternary polycationic polymers have been found to be especially useful.

5 The latter type of polymers appear to give slightly better water resistance than the former.

Finally, the second layer will contain from about 0.5 to about 5 percent by weight of a surfactant. For example, the amount of surfactant may be from about 1 to about 4 percent

10 by weight. As another example, the amount of surfactant may be from about 1 to about 3 percent by weight. Desirably, the surfactant will be a nonionic surfactant. For example, the nonionic surfactant may be a polyethoxylated alkylphenol.

The thickness of the second layer typically will be in

15 a range of from about 10 to about 50 micrometers. For example, the thickness of the second layer may be from about 15 to about 45 micrometers. As another example, the thickness of the second layer may be from about 20 to about 40 micrometers. However, thinner or thicker second layers may be

20 employed, if desired.

The second layer generally is formed on the first surface of the first layer by means which are well known to those having ordinary skill in the art. By way of illustration only, the layer may be formed by doctor blade; air knife;

25 Meyer rod; roll, reverse roll, and gravure coaters; brush applicator; or spraying. The second layer typically will be formed from a dispersion. The dispersion generally will have a viscosity of from about 0.005 to about 1 Pa s (5 to 1,000 centipoise) as measured with a Brookfield Viscometer, Model

30 LVT, using a No. 2 spindle at 30 rpm (Brookfield Engineering Laboratories, Inc., Stoughton, Massachusetts). For example, the dispersion may have a viscosity of from about 0.01 to about 0.5 Pa s (10 to 500 centipoise). As a further example, the dispersion may have a viscosity of from about 0.03 to

35 about 0.25 Pa s (30 to 250 centipoise).

In some embodiments, a third layer may be present; such layer will overlay the second surface of the first layer. The

layer may be, by way of illustration, a backsize coating. Such a coating generally consists essentially of a binder and clay. For example, the binder may be a polyacrylate, such as Rhoplex HA-16 (Rohm and Haas Company, Philadelphia, Pennsylvania). As another example, the clay may be Ultrawhite 90 (Englehard, Charlotte, North Carolina). A typical formulation would include the two materials in amounts of 579.7 parts by weight and 228.6 parts by weight, respectively. Water and/or a thickening agent will be added as necessary to give a final dispersion viscosity in the range of 0.100-0.140 Pa s (100-140 centipoise) at ambient temperature.

Also by way of illustration, the third layer may be a tie coat, i.e., a coating designed to bind a pressure-sensitive adhesive to the second surface of the first layer. A typical tie coat consists of a polyacrylate binder, clay, and silica. Alternatively, the third layer itself may be a pressure-sensitive adhesive. For example, a pressure-sensitive adhesive layer may consist of a styrene-butadiene copolymer, a poly(vinyl acetate), or a natural rubber. A pressure-sensitive adhesive layer typically will be present at a basis weight of from about 10 to about 40 gsm. When the third layer is a tie coat, a fifth layer consisting of a pressure-sensitive adhesive and overlaying the third layer also may be present.

In addition to or in place of the third layer, a fourth layer may be present. The fourth layer usually will be located between the first and second layers. The fourth layer typically will be formed from a dispersion consisting of, by way of example only, 208 parts by weight of Hycar® 26084 (B. F. Goodrich Company, Cleveland, Ohio), a polyacrylate dispersion having a solids content of 50 percent by weight (104 parts dry weight), 580 parts by weight of a clay dispersion having a solids content of 69 percent by weight (400 parts dry weight), and 100 parts by weight of water. Additional water and/or a thickening agent may be added as necessary to give a final dispersion viscosity in the range

of 0.100-0.140 Pa s (100-140 centipoise) at ambient temperature.

The present invention is further described by the examples which follow. Such examples, however, are not to be construed as limiting in any way either the spirit or the scope of the present invention.

In the examples, all ink jet printing evaluations were done using a Desk Jet 550 C color ink jet printer, Model C2121A, from Hewlett Packard Company, Camas, Washington. Two different test patterns were used to evaluate print sharpness, rate of ink drying, brilliance of color, and water resistance of the printed image. The first test pattern consisted of black fonts and a large solid-printed "C" (4.6 cm by 4.8 cm). The pattern was used to evaluate print coverage and evenness of ink application. The large printed area also allowed drying time comparisons. The second test pattern involved a four-color graphic print with large areas of red, green, blue, and yellow. This test pattern was used to evaluate the water resistance of the color prints.

Print quality testing consisted of three parts. First, ink absorption was estimated by printing characters in colored ink over one another. The printed area was rubbed with a finger and the degree of ink smearing was judged visually. The rate at which the printed sheet dried also was observed and recorded. Second, dot sharpness was determined by observing ink dots under a light microscope and observing smudging of the edge of the dot. Third, feathering was determined by observing diffusion of the ink into the substrate away from the dot by means of an 8-power magnification loop.

Coating adhesion was estimated by applying a strip of clear adhesive tape to the coated unprinted surface and applying fingertip pressure to the entire surface of the tape. The tape then was rapidly removed with a jerking motion. The amount of coating adhering to the tape surface was compared to other coated papers. Lower amounts of coating adhering to

the tape were indicative of stronger adhesion of the coating to the substrate surface.

Finally, water resistance was estimated by two methods. First, a drop of tap water was applied to the printed area and allowed to remain on the printed area for 3 to 5 seconds. The drop then was blotted and wiped away using Kleenex® tissue. The degree of smearing on the printed sheet was observed, as well as the amount of color transferred to the tissue. Each color was tested separately and evaluated. Second, the printed sheet was held under running tap water. The printed sheet was then blotted dry as described above and observed for color bleeding into adjacent areas as well as color transfer to the tissue.

15

#### Example 1

A polypropylene synthetic printing paper, Kimdura® FPG-110 Synthetic Printing Paper from Kimberly-Clark Corporation, Roswell, Georgia, was used as the base substrate or first layer. One side of the synthetic paper was coated with a composition consisting of 62 percent by weight (100 parts by weight) of a silica having an average particle size of 7.5 micrometers and a pore volume of 1.2 cc/g (Syloid 74X3500, W. R. Grace Company, Baltimore, Maryland), 31 percent by weight (50 parts by weight) latex binder (Airflex® 140, a vinyl acetate-ethylene copolymer available from Air Products, Allentown, Pennsylvania), 3 percent by weight (4.5 parts by weight) of a nonionic surfactant (Triton® X-405, a polyethoxylated octylphenol available from Union Carbide Corporation, Danbury, Connecticut), and 4 percent by weight (4 parts by weight) of a cationic polymer, an amide-epichlorohydrin copolymer (Reten 204LS supplied by Hercules Inc., Wilmington, Delaware). The resulting composition had a solids content of 28 percent by weight. The composition was applied at a basis weight of 17 grams per square meter (gsm) using a Meyer Rod and, upon drying, formed the second layer.

The coated substrate was evaluated for print quality, coating adhesion and water resistance as described earlier. The printed sheet had good ink absorption and dried rapidly. Dot sharpness was good and no feathering was observed. The sheet also had good coating adhesion. In the water resistance tests, the printed sheet had only slight smearing and slight color transfer.

#### Example 2

The procedure of Example 1 was repeated, except that the cationic polymer was a quaternary polycation synthetic organic polymer, Calgon 261 LV (Calgon Corporation, Pittsburgh, Pennsylvania). Print testing and adhesion results were the same as reported in Example 1, except that, in the water resistance tests, no smearing or color transfer were observed.

#### Example 3

The procedure of Example 1 was repeated, except that the first layer was an untreated cellulose web (30-lb. bond paper from Neenah Paper, a division of Kimberly-Clark Corporation, Neenah, Wisconsin). Print testing, second layer adhesion, and water resistance were the same as in Example 1.

#### Example 4

The procedure of Example 1 was repeated, except that first layer was a latex-saturated cellulose web. The web was formed from a blend of 89 percent by weight northern softwood pulp and 11 percent by weight of cedar pulp and had a basis weight of 54 gsm. The web was saturated with 18 parts of an acrylic latex per 100 parts of pulp on a dry weight basis. Print testing, adhesion, and water resistance were the same as in Example 1.

**Example 5**

One hundred parts by weight (64 percent by weight) of a calcium-modified silica pigment with an average particle size of 7.5 micrometers and a pore volume of 1.2 cc/g (SMR 3-729, W. R. Grace Company, Baltimore, Maryland), 50 parts by weight (32 percent by weight) of a cationic latex binder, a clay-reactive acrylic dispersion (Rhoplex P554, Rohm & Haas Company, Philadelphia, Pennsylvania), 4.5 parts by weight (3 percent by weight) of Triton® 405 surfactant, and 1 part of a modified cellulose viscosity modifier (Methocel 15A, Dow Chemical, Midland, Michigan) were blended together to give a coating composition containing 23 percent by weight solids.

Kimdura® FPG-110 was coated with the composition and tested as described in Example 1. The coated substrate showed very poor ink absorption and poor dot sharpness. Feathering was moderate. Coating adhesion was good, but water resistance was poor with moderate smearing and excessive color transfer to the tissue.

20

**Example 6**

The procedure of Example 5 was repeated, except that half (50 parts by weight) of the silica was replaced with the silica employed in Example 1. The resulting composition contained 33 percent by weight solids. The coated substrate had poor print quality and no water resistance.

25

**Example 7**

The procedure of Example 1 was repeated, except that the binder employed was Airflex® 125, an anionic vinyl acetate-ethylene copolymer (Air Products). The coated substrate had good print quality, but the water resistance testing showed slight smearing and slight color transfer.

30

**Example 8**

5 The procedure of Example 1 was repeated, except that the amount of cationic polymer was reduced to 5 parts by weight (3 percent by weight). The coated substrate had good print quality and coating adhesion, but the water resistance testing showed slight smearing and slight color transfer.

**Example 9**

10

The procedure of Example 1 was repeated, except that the amount of cationic polymer was reduced to 3 parts by weight (2 percent by weight). The coated substrate had good print quality and coating adhesion, but the water resistance testing  
15 showed moderate smearing and excessive color transfer.

**Example 10**

20 The procedure of Example 1 was repeated, except that the binder employed was a nonionic acrylic latex binder (Rhoplex® B-15P, Rohm & Haas Company). The composition coagulated and could not be used to coat the first layer.

**Example 11**

25

The procedure of Example 1 was repeated, except that the surfactant was replaced with Triton® X-100, a polyethoxylated octylphenol (Union Carbide Corporation). The resulting composition was too viscous for coating the substrate with a  
30 Meyer rod.

**Example 12**

35 The procedure of Example 1 was repeated, except that the surfactant was replaced with Triton® CF-10, a nonionic alkylaryl polyether (Union Carbide Corporation). The

resulting composition was too viscous for coating the substrate with a Meyer rod.

### Example 13

5

The procedure of Example 11 was repeated, except that the amount of Triton® CF-10 surfactant was reduced to 3 parts by weight (2 percent by weight). The coated substrate had good print quality and good coating adhesion. Water resistance testing showed no smearing and only very slight color transfer.

### Example 14

15

The procedure of Example 1 was repeated, except that the amount of surfactant was reduced to 3 parts by weight (2 percent by weight). The coated substrate had good print quality and good coating adhesion. Water resistance testing showed no smearing and no color transfer.

20

While the specification has been described in detail with respect to specific embodiments thereof, it will be appreciated that those skilled in the art, upon attaining an understanding of the foregoing, may readily conceive of alterations to, variations of, and equivalents to these embodiments. Accordingly, the scope of the present invention should be assessed as that of the appended claims and any equivalents thereto.

25



## WHAT IS CLAIMED IS:

1. A coated substrate comprising:  
a first layer having first and second surfaces; and  
a second layer overlaying the first surface of the first layer, which second layer is comprised of:  
5       an effective amount of a latex binder;  
          an effective amount of a hydrophilic silica;  
          an effective amount of a cationic polymer; and  
          an effective amount of a surfactant;  
in which the second layer has a pH of from about 2 to about  
10   6.
2. The coated substrate of claim 1, in which the amount of latex binder in the second layer is from about 20 to about 60 percent by weight, based on the total dry weight of the second layer.
3. The coated substrate of claim 2, in which the amount of latex binder in the second layer is from about 25 to about 40 percent by weight.
4. The coated substrate of claim 1, in which the amount of hydrophilic silica in the second layer is from about 20 to about 80 percent by weight, based on the total dry weight of the second layer.
5. The coated substrate of claim 4, in which the amount of hydrophilic silica in the second layer is from about 30 to about 70 percent by weight.
6. The coated substrate of claim 1, in which the amount of cationic polymer in the second layer is from about 1 to about 12 percent by weight, based on the total dry weight of the second layer.

7. The coated substrate of claim 6, in which the amount of cationic polymer in the second layer is from about 2 to about 8 percent by weight.
8. The coated substrate of claim 1, in which the amount of surfactant in the second layer is from about 0.5 to about 5 percent by weight, based on the total dry weight of the second layer.
9. The coated substrate of claim 8, in which the amount of surfactant in the second layer is from about 1 to about 4 percent by weight.
10. The coated substrate of claim 1, in which the hydrophilic silica has an average particle size no greater than about 20 micrometers.
11. The coated substrate of claim 10, in which the hydrophilic silica has an average particle size of from about 1 to about 20 micrometers.
12. The coated substrate of claim 10, in which the hydrophilic silica has an average particle size of from about 2 to about 13 micrometers.
13. The coated substrate of claim 1, in which the hydrophilic silica has a pore volume greater than 0.4 cc/g.
14. The coated substrate of claim 13, in which the hydrophilic silica has a pore volume of from about 1 to about 1.9 cc/g.
15. The coated substrate of claim 1, in which the first layer is a film or a nonwoven web.
16. The coated substrate of claim 15, in which the first layer is a cellulosic nonwoven web.

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 96/10939

**A. CLASSIFICATION OF SUBJECT MATTER**  
IPC 6 B41M5/00

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)  
IPC 6 B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP,A,0 487 350 (XEROX CORPORATION) 27 May 1992 see example 1	1
P,X	EP,A,0 661 168 (CANON KABUSHIKI KAISHA) 5 July 1995 see example 48	1
A	EP,A,0 594 896 (AGFA-GEVAERT) 4 May 1994 see the whole document	1
A	EP,A,0 529 110 (OJI YUKA GOSEISHI CO.) 3 March 1993 see page 5, line 42 - page 6, line 11	1
P,X	US,A,5 501 902 (F KRONZER) 26 March 1996 see the whole document	1

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

\* Special categories of cited documents:

- \*A\* document defining the general state of the art which is not considered to be of particular relevance
- \*E\* earlier document but published on or after the international filing date
- \*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- \*O\* document referring to an oral disclosure, use, exhibition or other means
- \*P\* document published prior to the international filing date but later than the priority date claimed

- \*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- \*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- \*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- \*A\* document member of the same patent family

Date of the actual completion of the international search

16 October 1996

Date of mailing of the international search report

04.12.1996

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+ 31-70) 340-2040, Tx. 31 651 epo nl,  
Fax: (+ 31-70) 340-3016

Authorized officer

Heywood, C

# INTERNATIONAL SEARCH REPORT

information on patent family members

International Application No

PCT/US 96/10939

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP-A-487350	27-05-92	US-A- 5270103 CA-A, C 2051205 DE-D- 69117884 DE-T- 69117884 JP-A- 4269582	14-12-93 22-05-92 18-04-96 26-09-96 25-09-92
EP-A-661168	05-07-95	JP-A- 8118787 JP-A- 8025794 JP-A- 7266689 AU-A- 8182694 CA-A- 2138734 CN-A- 1115284 JP-A- 7257017	14-05-96 30-01-96 17-10-95 06-07-95 29-06-95 24-01-96 09-10-95
EP-A-594896	04-05-94	NONE	
EP-A-529110	03-03-93	JP-A- 4077530 US-A- 5204188	11-03-92 20-04-93
US-A-5501902	26-03-96	CA-A- 2145891	29-12-95